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On the use of the quasi-Gaussian entropy theory in noncanonical ensembles. I. Prediction of temperature dependence of thermodynamic properties

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In previous articles we derived and tested the quasi-Gaussian entropy theory, a description of the excess Helmholtz free energy in terms of the potential energy distribution, instead of the configurational partition function. We obtained in this way the temperature dependence of thermodynamic functions in the canonical ensemble assuming a Gaussian, Gamma or Inverse Gaussian distribution. In this article we extend the theory to describe the temperature dependence of thermodynamic properties in an exact way in the isothermal-isobaric and grand canonical ensemble, using the distribution of the appropriate heat function. For both ensembles restrictions on and implications of these distributions are discussed, and the thermodynamics assuming a Gaussian or (diverging) Gamma distribution is derived. These cases have been tested for water at constant pressure, and the results for the latter case are satisfactory. Also the distribution of the heat function of some theoretical model systems is considered. © *1998 American Institute of Physics.* [S0021-9606(98)50232-2]

I. INTRODUCTION

The prediction of the temperature and density behavior of realistic fluidlike molecular systems based on an exact statistical mechanical approach is both very challenging and important for practical applications and the prediction of equations of state. For molecules in the ideal gas phase it is well possible to derive the thermodynamic functions in this way, see for example Frenkel *et al.*[1] On the contrary, the evaluation of the partition function for systems with interacting molecules is in general extremely difficult, and often severe approximations have to be made.

However, for the evaluation of macroscopic thermodynamic properties of realistic systems most of the information which is present in the partition function is redundant. It is sufficient to focus on the distribution of the appropriate fluctuations in the system.

Using this idea we have derived and applied in previous papers[2–4] the quasi-Gaussian entropy (QGE) theory to obtain the temperature dependence of thermodynamic properties at constant volume, based on the internal energy fluctuations of the system. It is possible in the canonical ensemble to focus on excess (''ideal reduced'') properties with respect to a proper reference. We showed that the ideal reduced Helmholtz free energy and entropy can be expressed in an exact way in terms of the excess internal energy distribution, which must be close to a Gaussian for macroscopic systems. Since the type of (model) distribution determines the free energy and all other derived thermodynamic functions, it hence determines the *statistical state* of the system. To derive the temperature dependence, an ordinary differential equation, the *thermodynamic master equation* (TME) was formulated. Assuming a Gamma or Inverse Gaussian distribution, the resulting solutions of the TME provide the temperature dependence of all properties based on the knowledge of a limited set of data at one initial reference temperature and agree very well with experimental data (water, methane, methanol) for all densities except in the vicinity of the critical point, that we did not investigate yet, and in multiphasic conditions.

However, the extension of the theory in this form using excess properties gives problems in other ensembles. Especially the definition of a proper general reference turns out to be difficult. Hence up to now this theory has been used only in an approximate way to describe temperature dependence in noncanonical ensemble conditions.[5,6]

In this paper we will describe how to extend the quasi-Gaussian entropy theory to obtain the temperature dependence of the thermodynamic functions in the isothermal-isobaric and grand canonical ensemble in an exact way. This is accomplished by using a different reference state and distributions of full thermodynamic properties (internal energy, enthalpy) instead of excess ones. Possible drawbacks can arise from the fact that the distributions required to describe full thermodynamic properties with high accuracy may be more complex than the ones needed for excess properties. In addition we will therefore also describe the use of a proper excess enthalpy in the *NpT* ensemble. An advantage of the new reference states is the fact that we immediately obtain expressions for the thermodynamic functions without explicitly solving the appropriate TME.

In a similar way we can also obtain the density dependence of thermodynamic properties using the distribution of

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the volume or number of particles within the QGE theory. This will be described in a separate paper.[7]

This article is organized as follows.

In order to avoid that the general idea gets obscured by ''technical'' details and specific applications in various ensembles, the basic principles of the QGE theory (both in the previous form[2–6] and the one described in this and the following article[7]) are summarized in Sec. II: The system and the choice of the reference state(s), the relation between free energy and the distribution of an extensive quantity (heat function, volume, number of particles) via the moment generating or cumulant generating function of that distribution, the statistical state of a system, the relation between parameters of the (model) distribution and thermodynamic input data and the derivation of related thermodynamic functions. Moreover, a unified notation for thermodynamic properties in the *NVT*, *NpT* and μVT ensembles is introduced.

In Sec. III we will describe the temperature dependence of thermodynamic functions at constant pressure (*NpT*) and constant chemical potential (μVT), using the unified notation. We introduce the definitions of the system and the reference state in Sec. III A and derive an expression of the free energy difference in terms of the distribution of the heat function. In Sec. III B we focus on the characteristics of this distribution and the way the parameters can be obtained. We indicate in Sec. III C how other thermodynamic functions may be obtained from the free energy function. Next a description of some important model distributions (Gaussian, Gamma and diverging Gamma) and associated statistical states is presented in Sec. III D. Finally, some remarks are made on the use of the new and the previous form of the QGE theory in the *NVT* ensemble (Sec. III E) and a possible exact use of excess fluctuations in the *NpT* ensemble (Sec. III F).

Applications to water of the various statistical states are presented in Sec. IV, along with some results on model systems (harmonic oscillators, ideal gas). Finally, in Sec. V we give some conclusions.

II. BASIC PRINCIPLES

As is well-known, because of the structure of statistical mechanics and especially of the semiclassical partition function, various free energy differences may be written in the form

$$\ln\langle e^{t\mathscr{X}}\rangle = \ln \int e^{t\mathscr{X}}\rho(\mathscr{X})d\mathscr{X}, \tag{1}$$

where $\mathscr{X}$ is some instantaneous extensive property (e.g., the internal or potential energy, enthalpy, volume, etc.), t is an intensive property (e.g., $\beta = 1/kT$), $\langle\cdots\rangle$ denotes an expectation value in the appropriate ensemble and $\rho(\mathscr{X})$ is the probability distribution function (''distribution'') of $\mathscr{X}$. As usual we denote instantaneous properties by calligraphic symbols, whereas thermodynamic averages are denoted by usual capitals. The precise nature of t and $\mathscr{X}$ depends on (a) the statistical ensemble (*NVT*, *NpT* or μVT), (b) the choice of the reference state and (c) the choice in which state (the actual system or reference) we evaluate the expectation value $\langle e^{t\mathscr{X}}\rangle$. This will be briefly illustrated below. A more detailed treatment can be found in Sec. III A, in Sec. II A of Ref. 7 and in previous papers.[2,4]

In the *NVT* ensemble, for example, we can define a reference state at the same temperature and density with the same Hamiltonian except for the classical inter and intramolecular interactions which are switched off.[4] The excess or *confined ideal reduced* Helmholtz free energy A^* can be written as

$$\beta A^* = \beta(A - A_{*\mathrm{ref}}) = \ln\langle e^{\beta\mathscr{U}'}\rangle = -\ln\langle e^{-\beta\mathscr{U}'}\rangle_{*\mathrm{ref}}, \tag{2}$$

where $\mathscr{U}'$ is the instantaneous ideal reduced internal energy (basically the classical potential energy). Here $\mathscr{X} = \mathscr{U}'$ and $t = \beta$ or $-\beta$, depending on whether the expectation value is evaluated in the actual system or reference ensemble ($*$ref).

In this paper (Sec. III A) we will show that in the *NVT* ensemble we can write the Helmholtz free energy difference between two ''temperatures'' β and β_0 as

$$\Delta(\beta A) = \beta A - \beta_0 A_0 = \ln\langle e^{\Delta\beta\mathscr{U}}\rangle_\beta = -\ln\langle e^{-\Delta\beta\mathscr{U}}\rangle_{\beta_0}, \tag{3}$$

where $\mathscr{X} = \mathscr{U}$ is the instantaneous internal energy and, depending on calculating $\langle e^{t\mathscr{X}}\rangle$ in the β or β_0 ensemble, $t = \beta - \beta_0 = \Delta\beta$ or $-\Delta\beta$.

In Ref. 7 we demonstrate that in the *NpT* ensemble we can define the Gibbs free energy difference between two pressures p and p^0 as

$$\beta\Delta G = \beta(G(p) - G(p^0)) = \ln\langle e^{\beta\Delta p\mathscr{V}}\rangle_p = -\ln\langle e^{-\beta\Delta p\mathscr{V}}\rangle_{p^0}, \tag{4}$$

where $\mathscr{X} = \mathscr{V}$ is the instantaneous volume and $t = \beta(p - p^0) = \beta\Delta p$ or $-\beta\Delta p$.

In all cases, the expectation value $\langle e^{t\mathscr{X}}\rangle$ and hence the free energy difference and all other thermodynamic properties can be evaluated once we know the distribution $\rho(\mathscr{X})$. In fact, $\langle e^{t\mathscr{X}}\rangle = G_{\mathscr{X}}(t) = \int e^{t\mathscr{X}}\rho(\mathscr{X})d\mathscr{X}$ is the *moment generating function*[8,9] (MGF) of the distribution $\rho(\mathscr{X})$ and $G_{\Delta\mathscr{X}}(t) = \langle e^{t\Delta\mathscr{X}}\rangle = e^{-tX}G_{\mathscr{X}}(t)$ is the *central moment generating function* where $\Delta\mathscr{X} = \mathscr{X} - X$ and $X = \langle\mathscr{X}\rangle$. The logarithm of the MGF is called the *cumulant generating function*[8–10] (CGF) of $\rho(\mathscr{X})$. Since the precise distribution is not known exactly for an arbitrary system, the CGF is often expanded in a Taylor series in t, obtaining a so-called *cumulant expansion*. Because the distribution is close to a Gaussian for macroscopic systems this expansion is usually truncated after the second, third or fourth order. Zwanzig's high temperature expansion[11] is basically such a cumulant expansion. Recently, cumulant expansions have also been used to obtain free energy differences by Molecular Dynamics or Monte Carlo simulations.[12–18] However, in the QGE theory we do not use such an expansion, but focus on the complete distribution.

Based on physical and mathematical principles we can formulate several restrictions on the possible model distributions $\rho(\mathscr{X})$, see Ref. 2, Sec. III B of this paper and Secs. II E and II F of Ref. 7. Acceptable model distributions are for example the Gaussian, Gamma and Inverse Gaussian distributions. The n unknown parameters of the distribution can be obtained by the method of moments,[9,19] i.e., equating the

TABLE I. Notation of different properties in various ensembles, where in general x, y, and z are the independent variables, λ is the appropriate label, F, W, S and C are the thermodynamic potential (free energy), heat function, entropy and heat capacity, Y and Z are ''conjugated'' properties and Υ is the partition function. $J=-pV$ and $D=U-\mu N$ are the grand potential and grand canonical heat function, see Eqs. (11) and (13). For completeness we also included the canonical ensemble, see also Sec. III E.

Ensemble	x	y	z	λ	F	W	S	C	$Y=\left(\frac{\partial F}{\partial y}\right)_{T,z}$	$Z=\left(\frac{\partial F}{\partial z}\right)_{T,y}$	Υ
Isothermal-isobaric	T	p	N	p	G	H	S	C_p	V	μ	Δ
Grand canonical	T	μ	V	μ	J	D	S	C_μ	$-N$	$-p$	Ξ
Canonical	T	V	N	V	A	U	S	C_V	$-p$	μ	Q

first n theoretical moments $M_r[.\mathscr{Z}]=\langle(\Delta.\mathscr{Z})^r\rangle$ expressed in terms of the parameters and the first n sample moments, which can be related to thermodynamic input data at one state point via general statistical mechanical relations such as

$$M_2[\mathscr{U}]=kT^2C_V, \quad M_2[\mathscr{V}]=-kT(\partial V/\partial p)_T,$$

etc. The Gaussian distribution, for example, is characterized by the first two moments, the Gamma and Inverse Gaussian by the first three.

With the appropriate thermodynamic input data at one state point we can obtain the free energy difference at that state point. However, we can also obtain the temperature dependence of Eqs. (2) and (3) and the pressure dependence of Eq. (4) in the following way.

If we have used the reference state ensemble to evaluate the MGF, the distribution and its parameters are fixed at one state point. Hence we immediately obtain the temperature or pressure dependence of the free energy difference and all other derived thermodynamic functions.

If we have evaluated the MGF in the system ensemble, the distribution and hence its parameters are also temperature or pressure dependent, so we do not obtain an explicit expression. However, it turns out that with the help of general thermodynamic relations we can formulate in each case an ordinary differential equation, the *thermodynamic master equation* (TME), the solution of which provides the explicit temperature or pressure dependence.

The route using the reference state ensemble seems advantageous, although the thermodynamic input data may be difficult to obtain in that ensemble, e.g. see Eq. (2), where the reference state is rather unphysical. In that case the other route is more appropriate, at the expense of having to solve explicitly the TME (see Refs. 2 and 4).

Since by either one of the two routes we obtain the free energy difference and derived thermodynamic properties as a function of an intensive parameter (e.g., β or p), and the relation between distribution and free energy is unique (Eq. (1) is a Laplace transform of the distribution) the distribution completely determines the thermodynamics of the system and therefore the *statistical state*.

In order to facilitate the derivations we introduce a unified notation for quantities in various ensembles, see Table I. In this way we can derive the temperature dependence using Eq. (3) for all three ensembles simultaneously (Sec. III).

III. THEORY

A. Definition of the system and reference state

The Gibbs free energy in the isothermal-isobaric ensemble (NpT) is given by

$$G=-kT\ \ln\ \Delta \tag{5}$$

with

$$\Delta=\int_0^\infty \frac{d\mathscr{V}}{v}e^{-\beta p\mathscr{V}}Q(N,\mathscr{V},T)$$

$$=\frac{h^{-d_N}}{vN!}\int_0^\infty d\mathscr{V}\int' d\mathbf{p}^N\sum_l \int'^{*}_{\mathscr{V}} d\mathbf{x}^N e^{-\beta\mathscr{H}} \tag{6}$$

and

$$\mathscr{H}=\mathscr{U}+p\mathscr{V}, \tag{7}$$

the isothermal-isobaric partition function and the instantaneous enthalpy, respectively. As in previous articles[2–6] we will use calligraphic symbols for instantaneous properties and usual roman symbols for thermodynamic averages. Furthermore,

$$Q(N,V,T)=\frac{h^{-d_N}}{N!}Q^e(N,T)\int' d\mathbf{p}^N\sum_l \int'^{*}_{V} d\mathbf{x}^N e^{-\beta\mathscr{U}} \tag{8}$$

is the canonical partition function, where h is Planck's constant, d_N and $Q^e(N,T)$ are the number of degrees of freedom and the electronic partition function for N molecules, assumed to be independent of the volume, $\mathscr{U}(\mathbf{x},\mathbf{p},l,N)$ the (instantaneous) internal energy and $\mathbf{x}^N$ and $\mathbf{p}^N$ the coordinates and conjugated momenta of N molecules. $\beta=1/kT$, with k the Boltzmann constant and the summation runs over all accessible vibrational states $\{l\}$. The prime and the star on the integrals denote the restrictions due to fixed bond length and bond angle constraints and the restrictions due to a possible confinement of the system within a part of configurational space, respectively.[4] Furthermore $\mathscr{V}$ is the instantaneous volume and p the pressure. The factor v in Eq. (6) is in fact a numerical volume differential, which arises from the definition of the entropy in the NpT ensemble with continuous volume; it makes Δ dimensionless and assures that in the zero temperature limit the entropy correctly tends to zero.[20] In fact, v is a measure of the accuracy with which we want to describe our macroscopic properties. However,

from Eqs. (5) and (6) it follows that free energy differences are independent of v. It is worth to note, since this was not explicitly mentioned in previous papers, that for polyatomic molecules in the canonical partition function the correction for the phase-space positions which are permutations of identical particles, should not only involve molecular permutations $(1/N!)$ but also the possible rotations and intramolecular displacements which are permutations of identical atoms of single molecules. In fact, the correction factor in the partition function should be $(N!(1+\gamma)^N)^{-1}$, where $\gamma \geqslant 0$ is a positive constant characteristic of the molecule, see the Appendix. For sake of simplicity in this paper, as in the previous ones, we have always included the factor $(1+\gamma)^{-N}$ into the electronic partition function.

The Gibbs free energy difference between two ''temperatures'' β and β_0 can now be expressed as

$$\begin{aligned}\Delta(\beta G) &= \beta G - \beta_0 G_0 \\ &= -\ln \frac{\int_0^\infty d\mathscr{V} \int' d\mathbf{p}^N \Sigma_l \int'^{*}_{\mathscr{V}} d\mathbf{x}^N e^{-\beta \mathscr{H}}}{\int_0^\infty d\mathscr{V} \int' d\mathbf{p}^N \Sigma_l \int'^{*}_{\mathscr{V}} d\mathbf{x}^N e^{-\beta_0 \mathscr{H}}} \\ &= H_0 \Delta\beta - \ln\langle e^{-\Delta\beta \Delta\mathscr{H}_0}\rangle_{\beta_0} \qquad (9) \\ &= H\Delta\beta + \ln\langle e^{\Delta\beta\Delta\mathscr{H}}\rangle, \qquad (10)\end{aligned}$$

where $H_0 = \langle \mathscr{H} \rangle_{\beta_0}$, $H = \langle \mathscr{H} \rangle$, $\Delta\mathscr{H}_0 = \mathscr{H} - H_0$ and $\Delta\mathscr{H} = \mathscr{H} - H$ with $\langle \cdots \rangle_{\beta_0}$ and $\langle \cdots \rangle$ ensemble averages in the β_0 and β ensemble.

In the grand canonical ensemble (μVT) the ''grand potential'' $J = -pV$ is

$$J = -kT \ln \Xi \qquad (11)$$

with

$$\begin{aligned}\Xi &= \sum_{\mathscr{N}=0}^{\infty} e^{\beta\mu\mathscr{N}} Q(\mathscr{N}, V, T) \\ &= \sum_{\mathscr{N}=0}^{\infty} \frac{h^{-d_{\mathscr{N}}}}{\mathscr{N}!} Q^e(\mathscr{N}, T) \int' d\mathbf{p}^{\mathscr{N}} \sum_l \int'^{*}_V d\mathbf{x}^{\mathscr{N}} e^{-\beta\mathscr{D}}, \qquad (12)\end{aligned}$$

$$\mathscr{D} = \mathscr{U} - \mu\mathscr{N}, \qquad (13)$$

the grand canonical partition function and the instantaneous grand canonical heat function (''granthalpy''), respectively. $\mathscr{N}$ is the instantaneous number of molecules in the system and μ the chemical potential. Also in this case we can express the free energy difference as

$$\begin{aligned}\Delta(\beta J) &= \beta J - \beta_0 J_0 \\ &= -\ln \frac{\Sigma_{\mathscr{N}=0}^{\infty} (h^{-d_{\mathscr{N}}}/\mathscr{N}!) \int' d\mathbf{p}^{\mathscr{N}} \Sigma_l \int'^{*}_V d\mathbf{x}^{\mathscr{N}} e^{-\beta\mathscr{D}}}{\Sigma_{\mathscr{N}=0}^{\infty} (h^{-d_{\mathscr{N}}}/\mathscr{N}!) \int' d\mathbf{p}^{\mathscr{N}} \Sigma_l \int'^{*}_V d\mathbf{x}^{\mathscr{N}} e^{-\beta_0\mathscr{D}}} \\ &= D_0 \Delta\beta - \ln\langle e^{-\Delta\beta\Delta\mathscr{D}_0}\rangle_{\beta_0} \qquad (14) \\ &= D\Delta\beta + \ln\langle e^{\Delta\beta\Delta\mathscr{D}}\rangle, \qquad (15)\end{aligned}$$

where $D_0 = \langle \mathscr{D} \rangle_{\beta_0}$, $D = \langle \mathscr{D} \rangle$, $\Delta\mathscr{D}_0 = \mathscr{D} - D_0$ and $\Delta\mathscr{D} = \mathscr{D} - D$.

So, denoting in general the free energy, heat function and entropy by F, W and S (see Table I), we have using the β_0 ensemble

$$\Delta(\beta F) = W_0 \Delta\beta - \ln\langle e^{-\Delta\beta\Delta\mathscr{W}_0}\rangle_{\beta_0}, \qquad (16)$$

whence

$$F(T) = W_0 - TS_0 - kT \ln\langle e^{-\Delta\beta\Delta\mathscr{W}_0}\rangle_{\beta_0}. \qquad (17)$$

Other thermodynamic properties follow simply as temperature derivatives:

$$S(T) = -\left(\frac{\partial F(T)}{\partial T}\right)_{y,z}, \qquad (18)$$

$$W(T) = F(T) + TS(T), \qquad (19)$$

$$C(T) = \left(\frac{\partial W(T)}{\partial T}\right)_{y,z}, \qquad (20)$$

with C, y and z the appropriate heat capacity and fixed properties, see Table I.

B. Distribution of the heat function

The term $\ln\langle e^{-\Delta\beta\Delta\mathscr{W}_0}\rangle_{\beta_0}$ can be written as

$$\ln\langle e^{-\Delta\beta\Delta\mathscr{W}_0}\rangle_{\beta_0} = \ln \int e^{-\Delta\beta\Delta\mathscr{W}_0} \rho_0(\Delta\mathscr{W}_0) d\Delta\mathscr{W}_0, \qquad (21)$$

with $\rho_0(\Delta\mathscr{W}_0)$ the probability distribution of the fluctuations $\Delta\mathscr{W}_0$ in the β_0-ensemble. In fact, ρ_0 is a continuous probability density, since in the quasiclassical limit $\mathscr{U}$, $\mathscr{H}$ and $\mathscr{D}$ are continuous. Since we can subdivide a macroscopic system into n identical, independent subsystems, each with linear dimension L larger than the typical correlation length[21,22] and $n \to \infty$, we can apply the central limit theorem[8,23,24] to show that $\rho_0(\Delta\mathscr{W}_0)$ is unimodal and close to a Gaussian distribution (''quasi-Gaussian''). Such a condition might not be fulfilled in the critical point region, where the correlation length tends to infinity, and hence the distribution is not necessarily well modeled by a unimodal one. However, the fact that everywhere else in the phase diagram the system can be described by unimodal distributions suggests that even at the critical point the distribution can be considered at least as a limit condition of a general (highly complex) unimodal distribution. The term $\langle e^{-\Delta\beta\Delta\mathscr{W}_0}\rangle_{\beta_0} \equiv G^0_{\Delta\mathscr{W}_0}(-\Delta\beta)$ is in fact the central moment generating function[8,9] of the distribution $\rho_0(\Delta\mathscr{W}_0)$. The zero superscript on $G^0_{\Delta\mathscr{W}_0}$ denotes the reference state condition. The distribution is statistical mechanically defined as

$$\rho_0(\Delta\mathscr{W}_0) = \frac{\Omega^*_{\Delta\mathscr{W}_0} e^{-\beta_0(W_0 + \Delta\mathscr{W}_0)}}{\Upsilon_0}, \qquad (22)$$

where Υ_0 is the appropriate partition function (Table I) evaluated at β_0, and

$$\Omega^*_{\Delta\mathscr{H}_0}=\frac{h^{-d_N}}{vN!}Q^e(N)\int_0^\infty d\mathscr{V}\int' d\mathbf{p}^N \times\sum_l \int'^*_{\mathscr{V}} d\mathbf{x}^N\delta(\Delta\mathscr{H}_0(\mathbf{x},\mathbf{p},l,\mathscr{V})-\Delta\mathscr{H}_0), \tag{23}$$

$$\Omega^*_{\Delta\mathscr{D}_0}=\sum_{\mathscr{N}=0}^{\infty}\frac{h^{-d_\mathscr{N}}}{\mathscr{N}!}Q^e(\mathscr{N})\int' d\mathbf{p}^\mathscr{N} \times\sum_l \int'^*_V d\mathbf{x}^\mathscr{N}\delta(\Delta\mathscr{D}_0(\mathbf{x},\mathbf{p},l,\mathscr{N})-\Delta\mathscr{D}_0), \tag{24}$$

are the appropriate ''volumes'' of the hypersurface in phase space of constant $\Delta\mathscr{H}_0$ or $\Delta\mathscr{D}_0$ with $\delta(\cdot)$ the Dirac delta function. We therefore find[4]

$$\frac{d\rho_0}{d\Delta\mathscr{W}_0}=-\rho_0\left[\beta_0-\frac{\partial\ln\Omega^*_{\Delta\mathscr{W}_0}}{\partial\Delta\mathscr{W}_0}\right]=-\rho_0\frac{(\Delta\mathscr{W}_0-\Delta\mathscr{W}_{0m})P^m(\Delta\mathscr{W}_0)}{G^n(\Delta\mathscr{W}_0)} \tag{25}$$

by expanding the term between square brackets around the mode (maximum) of ρ_0 in a Padé approximant.[25,26] $\Delta\mathscr{W}_{0m}$ is the position of the mode of the distribution and

$$P^m(\Delta\mathscr{W}_0)=\sum_{i=0}^{m}a_{i,0}(\Delta\mathscr{W}_0)^i, \tag{26}$$

$$G^n(\Delta\mathscr{W}_0)=\sum_{j=0}^{n}b_{j,0}(\Delta\mathscr{W}_0)^j, \tag{27}$$

are polynomials of order m and n in $\Delta\mathscr{W}_0$, where without loss of generality we can set $a_{m,0}=1$. Note that the zero subscript on the coefficients $\{a_{i,0}\}$ and $\{b_{j,0}\}$ reflects that they are evaluated at β_0 and therefore temperature independent. Equation (25) represents the generalized Pearson system of distributions,[2,4,27–30] the solutions of which are distributions of increasing complexity. At this point several remarks have to be made.

First, the parameters $\{a_{i,0}\}$ and $\{b_{j,0}\}$ can be expressed[2] in terms of a set of central moments $M_{k,0}=\langle(\Delta\mathscr{W}_0)^k\rangle_{\beta_0}$, which in turn via statistical mechanics[2,31,32] can be expressed in terms of some thermodynamic derivatives at temperature $T_0=1/k\beta_0$. In fact, the central moments of W are related to the heat capacity and some temperature derivatives in the following way:[2]

$$M_{2,0}=(kT_0)[T_0C_0],$$

$$M_{3,0}=(kT_0)^2\left[T_0^2\left(\frac{\partial C_0}{\partial T}\right)_{y,z}+2T_0C_0\right], \tag{28}$$

$$\ldots,$$

where C_0 and $(\partial C_0/\partial T)_{y,z}$ are the values of C and $(\partial C/\partial T)_{y,z}$ at T_0. If $M_{r,0}$ is the highest order moment required to express the parameters $\{a_{i,0}\}$ and $\{b_{j,0}\}$, this corresponds to the knowledge of C_0 and derivatives up to $(\partial^{r-2}C_0/\partial T^{r-2})_{y,z}$. Hence for a specific distribution via Eqs. (17)–(21) the temperature dependence of F, W, S and C is completely determined by the knowledge of W_0, S_0 and the heat capacity C_0 and a limited set of temperature derivatives at one temperature T_0. Therefore, each different type of distribution defines a different *statistical state* of the system. Note that since we have used Eqs. (9) and (14) to express the thermodynamic properties in terms of the distribution in the β_0 ensemble, we do not explicitly have to solve a ''thermodynamic master equation,'' like in Refs. 2–6.

Secondly, from all the possible distributions arising from the basic differential equation, Eq. (25), we have to select the ones which are compatible with physical-mathematical restrictions,[2] like the fact that the distribution is unimodal and should be defined on the interval $[\Delta\mathscr{W}_{0,\min},\infty\rangle$, where $\Delta\mathscr{W}_{0,\min}$ is the finite lower limit of $\Delta\mathscr{W}_0$.[33] This restriction is not strictly necessary for the granthalpy in some special cases where $\mu>0$ and so $\rho_0(\Delta\mathscr{D}_0)$ could be defined on the interval $\langle-\infty,\infty\rangle$. In this paper we do not discuss these very unusual cases. Possible unimodal distributions already investigated are the Gaussian, Gamma and Inverse Gaussian distribution.[2–4,8] From Eqs. (9) and (14) it is clear that the free energy diverges if $\beta\to0$, because the volume integral and the summation over the number of particles, as well as the kinetic part of the partition function, tend to infinity in absence of the Boltzmann factor. For the same reason β_0 must be different from zero, too. In fact, the moment generating function of the distribution ρ_0, $G^0_\mathscr{W}(-\Delta\beta)=\langle e^{-\Delta\beta\mathscr{W}}\rangle_{\beta_0}$ must be finite for any finite β except for $\beta=0$, i.e., $-\Delta\beta=\beta_0$. Note that $\rho_0(\Delta\mathscr{W}_0)=\rho_0(\mathscr{W})$.

As previously discussed,[2] for all distributions $\rho(\xi)$ arising from the generalized Pearson system [Eqs. (25)–(27)] with $m+1>n$, the MGF $G_\xi(t)=\langle e^{t\xi}\rangle$ is finite for all values of $t=-\Delta\beta$. For distributions defined on the interval $[\Delta\mathscr{W}_{0,\min},\infty\rangle$ where $m+1<n$ the MGF always diverges and when $m+1=n$ the MGF is finite only for $t=-\Delta\beta<1/b_{n,0}$. Therefore if

$$1/b_{n,0}=t_d=\lim_{\beta\to0}-\Delta\beta=\beta_0 \tag{29}$$

(where t_d denotes the value of t at which the MGF diverges) the free energy will fulfil the requirement to be always finite except when $\beta\to0$. In fact, this eliminates the parameter $b_{n,0}$ and reduces the complexity of the solution. So for all the ''temperature lines'' the first possible exact distributions are the Gamma distribution ($m=0$, $n=1$) and Inverse Gaussian distribution (a degenerate $m=1$, $n=2$ solution[4]) with $1/b_{n,0}=\beta_0$, defining the *diverging Gamma* and *diverging Inverse Gaussian states*.

C. Derivation of conjugated properties

Using the appropriate distribution from the generalized Pearson system we obtain an explicit expression of $F(T;S_0,W_0,C_0,\partial C_0/\partial T,\ldots,\partial^{r-2}C_0/\partial T^{r-2})$, where the parameters of the distribution are determined by the moments up to $M_{r,0}$ ($r=2$ for a Gaussian or diverging Gamma, $r=3$ for a Gamma or Inverse Gaussian distribution). Subsequent temperature derivatives of this expression yield $S(T)$, $W(T)$ and $C(T)$, see Eqs. (18)–(20). However, further ''conju-

gated'' thermodynamic properties follow from derivatives in the other two independent variables y and z, see Table I:

$$Y=\left(\frac{\partial F}{\partial y}\right)_{T,z}, \tag{30}$$

$$Z=\left(\frac{\partial F}{\partial z}\right)_{T,y}. \tag{31}$$

Since the parameters $S_0, W_0, C_0, \partial C_0/\partial T, \ldots, \partial^{r-2}C_0/\partial T^{r-2}$ are also functions of y and z, we can obtain $Y(T)$ and $Z(T)$ via

$$Y(T)=\frac{\partial F}{\partial S_0}\left(\frac{\partial S_0}{\partial y}\right)_{T,z}+\sum_{l=-1}^{r-2}\frac{\partial F}{\partial f_{l,0}}\left(\frac{\partial f_{l,0}}{\partial y}\right)_{T,z}, \tag{32}$$

$$Z(T)=\frac{\partial F}{\partial S_0}\left(\frac{\partial S_0}{\partial z}\right)_{T,y}+\sum_{l=-1}^{r-2}\frac{\partial F}{\partial f_{l,0}}\left(\frac{\partial f_{l,0}}{\partial z}\right)_{T,y}, \tag{33}$$

where we have defined

$$f_{-1,0}=W_0; \quad f_{0,0}=C_0; \quad f_{1,0}=\left(\frac{\partial C_0}{\partial T}\right)_{y,z}, \tag{34}$$

etc. Using the Maxwell relations[4,32] we find

$$\left(\frac{\partial f_{l,0}}{\partial y}\right)_{T,z}=-l\left(\frac{\partial^{l+1}Y_0}{\partial T^{l+1}}\right)_{y,z}-T_0\left(\frac{\partial^{l+2}Y_0}{\partial T^{l+2}}\right)_{y,z}, \tag{35}$$

$$\left(\frac{\partial f_{l,0}}{\partial z}\right)_{T,y}=-l\left(\frac{\partial^{l+1}Z_0}{\partial T^{l+1}}\right)_{y,z}-T_0\left(\frac{\partial^{l+2}Z_0}{\partial T^{l+2}}\right)_{y,z}, \tag{36}$$

$$\left(\frac{\partial S_0}{\partial y}\right)_{T,z}=-\left(\frac{\partial Y_0}{\partial T}\right)_{y,z}, \tag{37}$$

$$\left(\frac{\partial S_0}{\partial z}\right)_{T,y}=-\left(\frac{\partial Z_0}{\partial T}\right)_{y,z}, \tag{38}$$

where obviously $\partial^0 Y_0/\partial T^0=Y_0$. Hence $Y(T)$ and $Z(T)$ are simply expressions of the form $Y(T;Y_0,\partial Y_0/\partial T,\ldots,\partial^r Y_0/\partial T^r)$ and $Z(T;Z_0,\partial Z_0/\partial T,\ldots,\partial^r Z_0/\partial T^r)$.

D. Statistical states

Next we will derive expressions for $F(T)$, $W(T)$, $S(T)$, $C(T)$, $Y(T)$ and $Z(T)$ for the Gaussian, Gamma and diverging Gamma state. The equations of the Inverse Gaussian and diverging Inverse Gaussian states can be obtained straightforwardly, but we omitted them because in most cases their behavior is almost indistinguishable from the corresponding Gamma expressions.[4] The way to solve Eqs. (17)–(21) for these distributions is mathematically very similar to the case previously described in the canonical ensemble using excess properties. Therefore we will only give here the final expressions and refer to Refs. 2 and 4 for further details.

For a *Gaussian state*, we use the fact that in general for a Gaussian distribution[2,4]

$$\rho(\Delta\xi)=\frac{1}{\sqrt{2\pi b_0}}\exp\left\{-\frac{(\Delta\xi)^2}{2b_0}\right\}, \tag{39}$$

where we defined $\Delta\xi=\xi-\langle\xi\rangle$, the cumulant generating function is

$$\ln G_{\Delta\xi}(t)=\ln\langle e^{t\Delta\xi}\rangle=\tfrac{1}{2}b_0t^2 \tag{40}$$

with $b_0=M_2$. In this case substituting $t=-\Delta\beta$, $\Delta\xi=\Delta\mathscr{W}_0$, $b_0=b_{0,0}=M_{2,0}$ and $M_{2,0}$ given by Eq. (28) we obtain

$$F(T)=W_0-T\left(S_0+\frac{1}{2}C_0\right)+T_0C_0\left(1-\frac{T_0}{2T}\right), \tag{41}$$

$$W(T)=W_0+T_0C_0\left(1-\frac{T_0}{T}\right), \tag{42}$$

$$S(T)=S_0+\frac{1}{2}C_0-\frac{1}{2}C_0\left(\frac{T_0}{T}\right)^2, \tag{43}$$

$$C(T)=C_0\left(\frac{T_0}{T}\right)^2, \tag{44}$$

where W_0, S_0 and C_0 are the values of W, S and C at the reference temperature $T_0=1/k\beta_0$. Furthermore, using Eq. (32) we find for the density-related properties (see Table I)

$$Y(T)=Y_0+B_{\lambda 1}\left(\frac{T}{T_0}-1\right)-B_{\lambda 2}\left(1-\frac{T_0}{T}\right), \tag{45}$$

where

$$B_{\lambda 1}=T_0\left(\frac{\partial Y_0}{\partial T}\right)_{y,z}+\frac{1}{2}T_0^2\left(\frac{\partial^2 Y_0}{\partial T^2}\right)_{y,z}, \tag{46}$$

$$B_{\lambda 2}=\frac{1}{2}T_0^2\left(\frac{\partial^2 Y_0}{\partial T^2}\right)_{y,z}, \tag{47}$$

and with Eq. (33) we obtain a similar expression for $Z(T)$, replacing Y by Z in Eqs. (45)–(47). Note that the Gaussian state, because of the very special properties of the Gaussian distribution, is equivalent to a second order cumulant expansion of $\Delta(\beta F)$ in $\Delta\beta$.

For a *Gamma state*, we use the fact that in general for a Gamma distribution[2,4]

$$\rho(\Delta\xi)=\frac{b_1(1/b_1^2)^{b_0/b_1^2}}{\Gamma(b_0/b_1^2)}(b_0+b_1\Delta\xi)^{b_0/b_1^2-1}\times\exp\left\{-\frac{b_0+b_1\Delta\xi}{b_1^2}\right\} \tag{48}$$

with $\Gamma(\cdot)$ the Gamma function,[34] the cumulant generating function is

$$\ln G_{\Delta\xi}(t)=\ln\langle e^{t\Delta\xi}\rangle=-b_0\left[\frac{1}{b_1}t+\frac{1}{b_1^2}\ln(1-b_1t)\right] \tag{49}$$

with $b_0=M_2$ and $b_1=M_3/2M_2$. In this case substituting $t=-\Delta\beta$, $\Delta\xi=\Delta\mathscr{W}_0$, $b_0=b_{0,0}$, $b_1=b_{1,0}$, $M_2=M_{2,0}$ and $M_3=M_{3,0}$ we find with Eq. (28)

$$F(T)=W_0-\frac{T_0C_0}{\delta_{\lambda 0}}-TS_0+\frac{TC_0}{\delta_{\lambda 0}^2}[\delta_{\lambda 0}+\ln(1-\delta_{\lambda 0})]-\frac{TC_0}{\delta_{\lambda 0}^2}\ln(1-\delta_\lambda(T)), \tag{50}$$

$$W(T)=W_0+(T-T_0)C_0\left(\frac{\delta_\lambda(T)}{\delta_{\lambda 0}}\right), \tag{51}$$

$$S(T)=S_0-\frac{C_0}{\delta_{\lambda 0}^2}[\delta_{\lambda 0}+\ln(1-\delta_{\lambda 0})] + \frac{C_0}{\delta_{\lambda 0}^2}[\delta_\lambda(T)+\ln(1-\delta_\lambda(T))], \tag{52}$$

$$C(T)=C_0\left(\frac{\delta_\lambda(T)}{\delta_{\lambda 0}}\right)^2, \tag{53}$$

where we have defined

$$\delta_{\lambda 0}=\frac{b_{1,0}}{kT_0}=\frac{M_{3,0}}{2kT_0M_{2,0}}=\frac{T_0(\partial C_0/\partial T)_{y,z}}{2C_0}+1, \tag{54}$$

$$\delta_\lambda(T)=\frac{T_0\delta_{\lambda 0}}{T(1-\delta_{\lambda 0})+T_0\delta_{\lambda 0}}, \tag{55}$$

with $(\partial C_0/\partial T)_{y,z}$ the value of $(\partial C/\partial T)_{y,z}$ at T_0. Furthermore, from Eq. (32) we find after straightforward algebra

$$Y(T)=Y_0+B_{\lambda 1}\left(\frac{T}{T_0}-1\right)+B_{\lambda 2}\left(\frac{T}{T_0}-1\right)\frac{1-\delta_\lambda(T)}{1-\delta_{\lambda 0}} + B_{\lambda 3}\left(\frac{T}{T_0}\right)\ln\left(\frac{1-\delta_\lambda(T)}{1-\delta_{\lambda 0}}\right) \tag{56}$$

with

$$B_{\lambda 1}=T_0\left(\frac{\partial Y_0}{\partial T}\right)_{y,z}-\frac{4\delta_{\lambda 0}-3}{2\delta_{\lambda 0}^2}T_0^2\left(\frac{\partial^2 Y_0}{\partial T^2}\right)_{y,z} + \frac{1}{2\delta_{\lambda 0}^2}T_0^3\left(\frac{\partial^3 Y_0}{\partial T^3}\right)_{y,z}, \tag{57}$$

$$B_{\lambda 2}=-\frac{2\delta_{\lambda 0}-3}{2\delta_{\lambda 0}^2}T_0^2\left(\frac{\partial^2 Y_0}{\partial T^2}\right)_{y,z}+\frac{1}{2\delta_{\lambda 0}^2}T_0^3\left(\frac{\partial^3 Y_0}{\partial T^3}\right)_{y,z}, \tag{58}$$

$$B_{\lambda 3}=\frac{3\delta_{\lambda 0}-3}{\delta_{\lambda 0}^3}T_0^2\left(\frac{\partial^2 Y_0}{\partial T^2}\right)_{y,z}-\frac{1}{\delta_{\lambda 0}^3}T_0^3\left(\frac{\partial^3 Y_0}{\partial T^3}\right)_{y,z}, \tag{59}$$

and using Eq. (33) we obtain a similar expression for $Z(T)$, replacing Y by Z in Eqs. (56)–(59).

Finally, for a *diverging Gamma state* the restriction due to the divergence of the MGF at $\beta=0$ reduces the complexity of the solutions. In fact, combining the general expression of $b_{1,0}$ for a Gamma state,[2,4] $b_{1,0}=M_{3,0}/2M_{2,0}$, with Eq. (29), $b_{1,0}=1/\beta_0$, we obtain $M_{3,0}/2kT_0M_{2,0}\equiv\delta_{\lambda 0}=1$ and thus via Eq. (55) also $\delta_\lambda(T)=1$. This gives

$$F(T)=W_0-T_0C_0+T(C_0-S_0)+TC_0\ln\left(\frac{T_0}{T}\right), \tag{60}$$

$$W(T)=W_0+(T-T_0)C_0, \tag{61}$$

$$S(T)=S_0-C_0\ln\left(\frac{T_0}{T}\right), \tag{62}$$

$$C(T)=C_0, \tag{63}$$

and, after careful inspection[35]

$$Y(T)=Y_0+B_{\lambda 1}\left(\frac{T}{T_0}-1\right)+B_{\lambda 2}\left(\frac{T}{T_0}\right)\ln\left(\frac{T}{T_0}\right) \tag{64}$$

with

$$B_{\lambda 1}=T_0\left(\frac{\partial Y_0}{\partial T}\right)_{y,z}-T_0^2\left(\frac{\partial^2 Y_0}{\partial T^2}\right)_{y,z}, \tag{65}$$

$$B_{\lambda 2}=T_0^2\left(\frac{\partial^2 Y_0}{\partial T^2}\right)_{y,z}, \tag{66}$$

and using Eq. (33) a similar expression for $Z(T)$, replacing Y by Z in Eqs. (64)–(66).

E. Canonical ensemble

All derivations up to here are also valid for the canonical (*NVT*) ensemble, see also Table I. In that case we have to use the distribution of the full instantaneous internal energy $\mathscr{U}$. Any exact distribution in this ensemble must have a diverging MGF for $\beta\to 0$ as well, since the kinetic part of the Helmholtz free energy A tends to infinity for $T\to\infty$ (note, however, that the ideal reduced Helmholtz free energy A' is finite in this limit[4]). In previous papers[2–4] we showed that a formulation of the theory using the excess (''ideal reduced'') internal energy $\mathscr{U}'$ provides an excellent description of many systems at constant volume, already using a Gamma distribution. This already suggests that the description using the full internal energy $\mathscr{U}$ must be less successful than the description using the ideal reduced internal energy $\mathscr{U}'$ for the same type of distribution (i.e., level of the theory).

In fact, there are two general reasons for this: first it is very difficult to model the distribution of the energy which contains intramolecular quantum vibrational energy (which is not present in $\mathscr{U}'$), and secondly the kinetic energy (also not included in $\mathscr{U}'$) always requires as the simplest exact statistical state for the full energy a diverging Gamma, while for the ideal reduced energy a Gamma state of full complexity is the simplest exact solution.

Consider for example the isochoric heat capacity C_V. The first exact expression using the full internal energy is a diverging Gamma state, where from Eq. (63) we have $C_V(T)=C_{V0}$. Restricting ourselves for simplicity to monatomic molecules, we see that the ideal reduced heat capacity C_V', i.e., with respect to an ideal gas at the same density and temperature, is simply a constant

$$C_V'(T)=C_{V0}-\tfrac{3}{2}Nk. \tag{67}$$

However, using the ideal reduced internal energy distribution, we obtain for a Gamma state[2–4]

$$C_V'(T)=C_{V0}'\left(\frac{T_0}{T(1-\delta_0)+T_0\delta_0}\right)^2 \tag{68}$$

with

$$\delta_0=\frac{T_0(\partial C_{V0}'/\partial T)}{2C_{V0}'}+1 \tag{69}$$

which is clearly different, and moreover proved to be an excellent model of water, methane and methanol. Therefore

in the canonical ensemble we use the description in terms of the ideal reduced internal energy $\mathscr{U}'$ instead of the full energy $\mathscr{U}$.

F. Excess properties in the *NpT* ensemble

Compared to the canonical ensemble, it is much more difficult to define and use excess properties to set up the theory in the isothermal-isobaric ensemble. So far we were only able to derive the theory in that ensemble using excess properties in an approximated way.[5] Here we will illustrate how to define a proper reference state that can be used to derive the theory for fluctuations of an excess instantaneous enthalpy $\mathscr{H}^c$, where we have removed the intramolecular quantum vibrational and kinetic parts of the energy. Such a formally equivalent and exact derivation of the theory could be preferable from a practical point of view, since for a given level of the theory (defined by the type of statistical state we want to use to model the system) the excesslike heat functions might be described with higher accuracy as for the canonical ensemble, Sec. III E.

We can use the previously introduced general approximation for the canonical partition function[4]

$$Q \cong \frac{1}{N!} Q^e Q^{\mathrm{kin}} Q_{id}^v \int'^* d\mathbf{x}^N e^{-\beta \mathscr{U}'}, \tag{70}$$

with Q^{kin} the semiclassical kinetic partition function (including the factor h^{-d_N}), $\mathscr{U}' = \Phi + \Psi + \mathscr{E}^0 - E_{id}^0$ where Φ and Ψ are the inter and intramolecular classical potential energies, $\mathscr{E}^0$ is the overall vibrational ground state energy of the system and where E_{id}^0 and Q_{id}^v are the overall vibrational ground state energy and partition function of the ideal gas ($\Phi = 0$), respectively.

We define a reference state as an ideal gas with no classical inter and intramolecular potential energy ($\Phi = \Psi = 0$, so $\mathscr{E}^0 = E_{\mathrm{id}}^0$) where by an infinite attractive potential among the molecules the centers of mass of the molecules are confined within a small volume ''differential'' v, as well as the full volume of the system. The corresponding reference isothermal-isobaric partition function is

$$\Delta_{*\mathrm{ref}} = \frac{1}{N!} Q^e Q^{\mathrm{kin}} Q_{\mathrm{id}}^v Z_{\mathrm{id}}^{\mathrm{rot}} \frac{v^N v}{v} \int_{\mathrm{id}}'^* d\mathbf{x}_{\mathrm{int}}^N, \tag{71}$$

where the translational configurational volume is given by v^N, $Z_{\mathrm{id}}^{\mathrm{rot}} = (z_{\mathrm{id}}^{\mathrm{rot}})^N$ is the ideal gas rotational configurational volume and $\int_{\mathrm{id}}'^* d\mathbf{x}_{\mathrm{int}}^N = (\int_{\mathrm{id}}'^* d\mathbf{x}_{\mathrm{int}}^1)^N$ is the ideal gas configurational volume of the classical intramolecular coordinates $\mathbf{x}_{\mathrm{int}}^N$, for a given definition of the internal and rotational coordinates of the single molecule. The factor v/v arises from the integration over the volume. As usual[4] the prime and the star on the integrals denote the possible integration restrictions due to fixed bond lengths and angles and to a confinement of the system within a part of configurational space, here in the ideal gas condition. Note that the use of translational, rotational and intramolecular coordinates in Eq. (71) implies that also the kinetic partition function Q^{kin} is expressed using the conjugated momenta of these coordinates.

Hence the reference thermodynamic properties are

$$G_{*\mathrm{ref}} = -kT \ln \frac{1}{N!} Q^e Q^{\mathrm{kin}} Q_{\mathrm{id}}^v Z_{\mathrm{id}}^{\mathrm{rot}} \frac{v^N v}{v} \int_{\mathrm{id}}'^* d\mathbf{x}_{\mathrm{int}}^N, \tag{72}$$

$$S_{*\mathrm{ref}} = -\left(\frac{\partial G_{*\mathrm{ref}}}{\partial T}\right)_{p,N}, \tag{73}$$

$$H_{*\mathrm{ref}} = G_{*\mathrm{ref}} + TS_{*\mathrm{ref}}, \tag{74}$$

$$C_{p*\mathrm{ref}} = \left(\frac{\partial H_{*\mathrm{ref}}}{\partial T}\right)_{p,N}, \tag{75}$$

$$V_{*\mathrm{ref}} = \left(\frac{\partial G_{*\mathrm{ref}}}{\partial p}\right)_{T,N} = 0, \tag{76}$$

etc. We define the *corrected* thermodynamic properties as

$$G^c = G - G_{*\mathrm{ref}} = -kT \ln \frac{\int_0^\infty d\mathscr{V} e^{-\beta p \mathscr{V}} \int_{\mathscr{V}}'^* d\mathbf{x}^N e^{-\beta \mathscr{U}'}}{\int_{\mathrm{id}}'^* d\mathbf{x}_{\mathrm{int}}^N Z_{\mathrm{id}}^{\mathrm{rot}} v^N v}, \tag{77}$$

$$S^c = S - S_{*\mathrm{ref}} = -\left(\frac{\partial G^c}{\partial T}\right)_{p,N}, \tag{78}$$

$$H^c = H - H_{*\mathrm{ref}} = G^c + TS^c, \tag{79}$$

$$C_p^c = C_p - C_{p*\mathrm{ref}} = \left(\frac{\partial H^c}{\partial T}\right)_{p,N}, \tag{80}$$

$$V^c = V = \left(\frac{\partial G}{\partial p}\right)_{T,N}. \tag{81}$$

Defining the instantaneous corrected enthalpy $\mathscr{H}^c = \mathscr{U}' + p\mathscr{V}$, from the definition of the corrected properties we can write the corrected free energy difference in the same way as Eqs. (9) and (10):

$$\Delta(\beta G^c) = -\ln \frac{\int_0^\infty d\mathscr{V} \int'^* d\mathbf{x}^N e^{-\beta \mathscr{H}^c}}{\int_0^\infty d\mathscr{V} \int'^* d\mathbf{x}^N e^{-\beta_0 \mathscr{H}^c}}$$

$$= H_0^c \Delta\beta - \ln \langle e^{-\Delta\beta \Delta\mathscr{H}_0^c} \rangle_{\beta_0} \tag{82}$$

$$= H^c \Delta\beta + \ln \langle e^{\Delta\beta \Delta\mathscr{H}^c} \rangle_{\beta} \tag{83}$$

with $\Delta\mathscr{H}_0^c = \mathscr{H}^c - H_0^c$, $\Delta\mathscr{H}^c = \mathscr{H}^c - H^c$ with $H_0^c = \langle \mathscr{H}^c \rangle_{\beta_0}$ and $H^c = \langle \mathscr{H}^c \rangle$. From this follows

$$G^c = H_0^c - TS_0^c - kT \ln \langle e^{-\Delta\beta \Delta\mathscr{H}_0^c} \rangle_{\beta_0}. \tag{84}$$

From these equations it is evident that using the distribution of the instantaneous corrected enthalpy $\mathscr{H}^c$ in the β_0 ensemble,

$$\rho_0(\mathscr{H}^c) = \frac{e^{-\beta_0 \mathscr{H}^c} \int_0^\infty d\mathscr{V} \int_{\mathscr{V}}'^* d\mathbf{x}^N \delta(\mathscr{H}^c(\mathbf{x}, \mathscr{V}) - \mathscr{H}^c)}{\int_0^\infty d\mathscr{V} \int_{\mathscr{V}}'^* d\mathbf{x}^N e^{-\beta_0 \mathscr{H}^c}} \tag{85}$$

also fully defined by a set of moments of $\mathscr{H}^c$ or temperature derivatives of H^c, in the *NpT* ensemble all the considerations and derivations of Sec. III B–III D can be applied to the corrected thermodynamic properties by simply exchanging in every equation the full properties with the corresponding

corrected ones. For instance, for a diverging Gamma state (the formally exact Gamma state for both the corrected and full enthalpy fluctuations) we have

$$G^c(T)=H_0^c-T_0C_{p0}^c+T(C_{p0}^c-S_0^c)+TC_{p0}^c\ \ln\left(\frac{T_0}{T}\right), \quad (86)$$

$$H^c(T)=H_0^c+(T-T_0)C_{p0}^c, \quad (87)$$

$$S^c(T)=S_0^c-C_{p0}^c\ \ln\left(\frac{T_0}{T}\right), \quad (88)$$

$$C_p^c(T)=C_{p0}^c, \quad (89)$$

and

$$V(T)=V_0+B_{\lambda 1}^c\left(\frac{T}{T_0}-1\right)+B_{\lambda 2}^c\left(\frac{T}{T_0}\right)\ln\left(\frac{T}{T_0}\right), \quad (90)$$

with

$$B_{\lambda 1}^c=T_0\left(\frac{\partial V_0}{\partial T}\right)_{p,N}-T_0^2\left(\frac{\partial^2 V_0}{\partial T^2}\right)_{p,N}, \quad (91)$$

$$B_{\lambda 2}^c=T_0^2\left(\frac{\partial^2 V_0}{\partial T^2}\right)_{p,N}, \quad (92)$$

and using Eq. (33) a similar expression for $\mu^c(T)$, replacing V by μ^c in Eqs. (90)–(92). It is very useful to link the reference properties to ideal gas ones. From the ideal gas free energy

$$\begin{aligned}G_{\mathrm{id}}&=-kT\ \ln\frac{1}{N!}Q^eQ^{\mathrm{kin}}Q_{\mathrm{id}}^vZ_{\mathrm{id}}^{\mathrm{rot}}\int_{\mathrm{id}}'^{*}d\mathbf{x}_{\mathrm{int}}^Ne^{-\beta\Psi}\\&\quad\times\int_0^\infty\frac{d\mathscr{V}}{v}e^{-\beta p\mathscr{V}}\mathscr{V}^N\\&=-kT\ \ln\ Q^eQ^{\mathrm{kin}}Q_{\mathrm{id}}^vQ_{\mathrm{id}}^{\mathrm{rot}}\int_{\mathrm{id}}'^{*}d\mathbf{x}_{\mathrm{int}}^Ne^{-\beta\Psi}\frac{1}{v(\beta p)^{N+1}}\end{aligned} \quad (93)$$

we obtain after a few steps

$$G_{*\mathrm{ref}}=G_{\mathrm{id}}-NkT\ \ln\langle e^{\beta\psi}\rangle_{\mathrm{id}}-NkT\ \ln\left(\frac{pv}{NkT}\right)-NkT, \quad (94)$$

$$S_{*\mathrm{ref}}=S_{\mathrm{id}}+Nk\ \ln\langle e^{\beta\psi}\rangle_{\mathrm{id}}-\frac{N\langle\psi\rangle_{\mathrm{id}}}{T}+Nk\ \ln\left(\frac{pv}{NkT}\right), \quad (95)$$

$$H_{*\mathrm{ref}}=H_{\mathrm{id}}-N\langle\psi\rangle_{\mathrm{id}}-NkT, \quad (96)$$

$$C_{p*\mathrm{ref}}=C_{p\ \mathrm{id}}-N\left(\frac{\partial\langle\psi\rangle_{\mathrm{id}}}{\partial T}\right)_{p,N}-Nk, \quad (97)$$

where ψ is the molecular intramolecular potential with $\langle\Psi\rangle_{\mathrm{id}}=N\langle\psi\rangle_{\mathrm{id}}$ and $\langle e^{\beta\psi}\rangle_{\mathrm{id}}=\int_{\mathrm{id}}'^{*}d\mathbf{x}_{\mathrm{int}}^1/\int_{id}'^{*}e^{-\beta\psi}d\mathbf{x}_{\mathrm{int}}^1$ is the moment generating function of the molecular intramolecular potential energy fluctuation. In the case of small molecules where $\psi=0$ (e.g., water) the previous equations simplify even further.

It should be noted that for systems where no intramolecular potential is present and in the whole temperature range of interest the vibrations are largely confined to the ground state, if the corrected enthalpy fluctuations are properly modeled by a diverging Gamma state, also the full enthalpy fluctuations can be described by a diverging Gamma state. On the contrary, for any other discussed statistical state such correspondence is lost.

Finally it must be mentioned that in the grand canonical ensemble Eq. (70) cannot provide any derivation based on an excesslike granthalpy and so in that ensemble we can only use the full property.

IV. RESULTS

Before presenting a comparison between the Gamma state expressions and experimental data of water, we will first show that the Gamma distribution is the exact distribution for the heat function of two simple systems, i.e., the internal, kinetic and potential energy of a set of classical harmonic oscillators in the *NVT* ensemble and the enthalpy (internal energy) of an ideal gas in the *NpT* (*NVT*) ensemble.

First consider a set of N classical harmonic oscillators (e.g. normal modes) in the canonical ensemble. It is always possible to define a set of generalized coordinates ξ_i and momenta π_i (not necessarily conjugated) such that the instantaneous internal energy can be written as

$$\begin{aligned}\mathscr{U}&=\sum_{i=1}^N\frac{1}{2}\kappa_i\xi_i^2+\sum_{i=1}^N\frac{1}{2m_i}\pi_i^2\\&=\frac{kT}{2}\sum_{i=1}^N\left(\frac{\xi_i}{\sigma_{\xi_i}}\right)^2+\frac{kT}{2}\sum_{i=1}^N\left(\frac{\pi_i}{\sigma_{\pi_i}}\right)^2\\&=\frac{kT}{2}\sum_{i=1}^{2N}\left(\frac{\tau_i}{\sigma_{\tau_i}}\right)^2=\frac{kT}{2}\chi^2\end{aligned} \quad (98)$$

with κ_i and m_i force constants and reduced masses and where we used the fact that the variance of the position is $\sigma_{\xi_i}^2=kT/\kappa_i$ and that of the momenta is $\sigma_{\pi_i}^2=m_ikT$. Furthermore, τ_i denotes a general coordinate. Since $\mathscr{U}$ is the sum of squares of an independent standard normal variable τ_i/σ_{τ_i}, it is proportional to a χ^2 variable,[36] which follows a χ^2-distribution with in this case $2N$ degrees of freedom. Hence the distribution of $\mathscr{U}=(kT/2)\chi^2$ is a χ^2-distribution as well,[2,8]

$$\rho(\mathscr{U})=\frac{(1/kT)^N}{\Gamma(N)}\mathscr{U}^{N-1}e^{-\mathscr{U}/kT} \quad (99)$$

which is a special subfamily of Gamma distributions. In fact, it is a diverging Gamma distribution since $b_1=kT$ [cf. Eq. (48)].

Of course, the same argument can also be applied to the potential energy $\mathscr{U}_{\mathrm{pot}}=\Sigma_{i=1}^N(\kappa_i/2)\xi^2$ or the kinetic energy $\mathscr{K}=\Sigma_{i=1}^N(1/2m_i)p_i^2$ only, giving in both cases a χ^2-distribution with N degrees of freedom, i.e., a diverging Gamma distribution of the form

$$\rho(\mathscr{U}_{\rm pot})=\frac{(1/kT)^{N/2}}{\Gamma(N/2)}\,\mathscr{U}_{\rm pot}^{N/2-1}e^{-\mathscr{U}_{\rm pot}/kT} \tag{100}$$

$$\rho(\mathscr{K})=\frac{(1/kT)^{N/2}}{\Gamma(N/2)}\,\mathscr{K}^{N/2-1}e^{-\mathscr{K}/kT}. \tag{101}$$

The MGF of these distributions follows from Eq. (49), giving

$$G_{\mathscr{U}_{\rm pot}}=G_{\mathscr{K}}(t)=\left(\frac{\beta}{\beta_0}\right)^{N/2}=\left(\frac{\beta}{\beta-t}\right)^{N/2}, \tag{102}$$

where we defined $t=\Delta\beta$. Note that Eq. (100) is also in general the distribution of the kinetic energy in the canonical and isothermal-isobaric ensemble.

The second system is an ideal gas of N particles in the *NpT* ensemble. For simplicity we first consider a monatomic gas, and discuss polyatomic molecules afterwards. The isothermal-isobaric partition function for a monatomic ideal gas is given by[20]

$$\Delta_{\rm id}=\frac{(q^e)^N\Lambda^{-3N}}{v(\beta p)^{N+1}}, \tag{103}$$

where $\Lambda=\sqrt{h^2\beta/2\pi m}$ is the thermal wavelength with m the mass of the atom. Since $\Delta(\beta G)=\ln(\Delta_{\rm id,0}/\Delta_{\rm id})$, we have from Eq. (10)

$$G_{\mathscr{H}}(\Delta\beta)=\langle e^{\Delta\beta\mathscr{H}}\rangle=\frac{\Delta_{\rm id,0}}{\Delta_{\rm id}}=\left(\frac{\beta}{\beta_0}\right)^{(5/2)N+1}=\left(\frac{\beta}{\beta-t}\right)^{(5/2)N+1} \tag{104}$$

defining $t=\Delta\beta$. Note that from $\Delta_{\rm id}$ follows the ideal gas law[37] $pV=(N+1)kT$, so $H=(\frac{5}{2}N+1)kT$, and using the general relation[9] $G_{\Delta\mathscr{X}}(t)=e^{-tX}G_{\mathscr{X}}(t)$, we find

$$G_{\Delta\mathscr{H}}(t)=e^{-t[(5/2)N+1]/\beta}\left(\frac{\beta}{\beta-t}\right)^{(5/2)N+1}. \tag{105}$$

For a Gamma distribution $\rho(\xi)$ we have from Eq. (49) a similar expression

$$G_{\Delta\xi}(t)=e^{-t(b_0/b_1)}\left(\frac{1/b_1}{1/b_1-t}\right)^{b_0/b_1{}^2}. \tag{106}$$

Using $H=(\frac{5}{2}N+1)kT$, so $C_p=(\frac{5}{2}N+1)k$ and $\partial C_p/\partial T=0$, we obtain with $b_0=M_2$, $b_1=M_3/(2M_2)$ and Eq. (28)

$$\frac{1}{b_1}=\beta;\quad \frac{b_0}{b_1}=\left(\frac{5}{2}N+1\right)/\beta;\quad \frac{b_0}{b_1{}^2}=\frac{5}{2}N+1. \tag{107}$$

Since the moment generating function, being a Laplace transform, is uniquely related to the distribution,[9] this proves that the distribution of the enthalpy fluctuations for an ideal monatomic gas in the *NpT* ensemble is a diverging Gamma distribution ($b_1=kT$).

When we are dealing with a polyatomic ideal gas,

$$\Delta_{\rm id}=\frac{(q^e)^N\Lambda^{-3N}}{v(\beta p)^{N+1}}(q_{\rm id}^{\rm rot}q_{\rm id}^{\rm int})^N \tag{108}$$

with $q_{\rm id}^{\rm rot}$ and $q_{\rm id}^{\rm int}$ the ideal gas rotational and internal partition function per molecule. The rotational partition function is in general given by[38]

$$q_{\rm id}^{\rm rot}=\frac{\pi^{1/2}}{\sigma}\left(\frac{T^3}{\Theta_A\Theta_B\Theta_C}\right)^{1/2}=\frac{1}{\sigma}\left(\frac{\pi}{k^3\Theta_A\Theta_B\Theta_C}\right)^{1/2}\left(\frac{1}{\beta}\right)^{3/2} \tag{109}$$

with $\Theta_A,\Theta_B,\Theta_C$ the principal characteristic rotational temperatures and σ the symmetry number.

If the s internal degrees of freedom can be described classically within a harmonic approximation (e.g., harmonic bond and angle potentials), the distribution of the total enthalpy is still a diverging Gamma distribution, since in that case

$$q_{\rm id}^{\rm int}=\left(\frac{2\pi}{h\beta}\right)^s\prod_{i=1}^{s}\left(\frac{\mu_i}{\kappa_i}\right)^{1/2} \tag{110}$$

with μ_i and κ_i the appropriate reduced mass and force constant, and hence

$$G_{\mathscr{H}}(\Delta\beta)=\frac{\Delta_{\rm id,0}}{\Delta_{\rm id}}=\left(\frac{\beta}{\beta_0}\right)^{(5/2)N+1}\left(\frac{\beta}{\beta_0}\right)^{(3/2)N}\left(\frac{\beta}{\beta_0}\right)^{sN}=\left(\frac{\beta}{\beta-t}\right)^{(4+s)N+1}. \tag{111}$$

Note that in all these cases also the distribution of the corrected enthalpy fluctuations (Sec. III F) is exactly a diverging Gamma distribution. Even when quantum intramolecular vibrations are present and if the classical intramolecular interactions are absent or harmonic the corrected enthalpy fluctuations are still exactly described by a diverging Gamma state. This moreover suggests that a diverging Gamma state for the full or corrected enthalpy fluctuations might also be a good description for the temperature dependence of thermodynamic properties at constant pressure of *real* (dilute) gases. Note that the distribution of the internal energy $\mathscr{U}$ of a monatomic ideal gas in the *NVT* ensemble is a Gamma distribution too. For polyatomic molecules the same requirements as described above for the *NpT* ensemble are valid.

We tested the validity of the Gamma state description on water, using both full and corrected enthalpy fluctuations [Eqs. (60)–(66) and (86)–(92]. Experimental data at fixed pressure were taken from Schmidt[39] at 1, 50, 400 and 1000 bar and ideal gas properties from Frenkel *et al.*[1] The critical pressure is 221.2 bar. For the two lowest pressures a phase transition occurs, so adopting the usual thermodynamic approach we have in that case on both sides of the singularity two independent solutions, a gas and a liquid branch. At 400 bar the behavior in the vicinity of the critical temperature (647.3 K) is rather complex, so also there we used a ''liquid'' and a ''gas'' branch. At 1000 bar we only used the ''liquid'' branch. For the liquid solutions we used $T_0=313$ K, for the gas branches we used $T_0=613$ K (1 bar), 813 K (50 bar) and 1013 K (400 bar).

In Figs. 1–4 the predictions of the full enthalpy H and heat capacity C_p are given using the full enthalpy fluctuations [Eqs. (61) and (63)]. Since for the liquid side there is no divergence restriction, the parameters were calculated for a general Gamma state, obtaining in all cases $\delta_{p0}\cong 1$. We

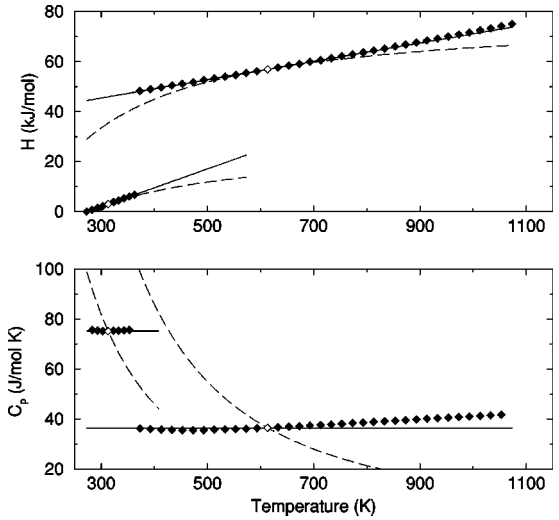

FIG. 1. Enthalpy H and heat capacity C_p along a water isobar at $p=1.0$ bar. Legend: experimental values (♦), diverging Gamma states [Eqs. (61) and (63)] on the liquid and gas side (——), and corresponding Gaussian states [Eqs. (42) and (44)] (— — —). The critical pressure is 221.2 bar (Ref. 39). The values of T_0 for the liquid and gas side are indicated by ◇.

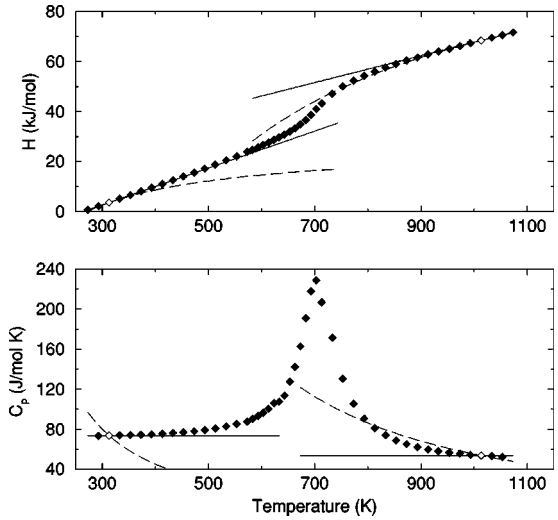

FIG. 3. Enthalpy H and heat capacity C_p along a water isobar at $p=400.0$ bar. Legend: see Fig. 1.

therefore used a diverging Gamma state, which according to the figures describes the liquid behavior for the two subcritical isobars very well up to the phase transition, or for the supercritical isobars roughly up to the critical temperature. For the gas side a diverging Gamma state is clearly a good description for temperatures starting somewhat above the phase transition (or ~150 K above the critical temperature for $p=400$ bar), as already suggested by the fact that the (corrected) enthalpy fluctuations of an ideal gas are exactly a diverging Gamma distribution, see Eq. (104). Obviously the complexity of a diverging Gamma state is not high enough to properly describe the behavior in the vicinity of the critical point at 400 bar, although from Fig. 4 it is clear that at a higher isobar (1000 bar) the behavior is much closer to a single diverging Gamma state in the whole temperature range. For comparison we also included the predictions of the Gaussian state [Eqs. (41)–(47)], which is equivalent to a second order cumulant expansion of $\Delta(\beta G)$ in $\Delta\beta$ (see Sec. II), using the same input data as the diverging Gamma state. From the figures it is clear that the Gaussian state, which has the same complexity as a diverging Gamma state (i.e., the same number of input data at T_0), is much worse, especially evident from the heat capacity. The use of a physically acceptable Gamma distribution function hence gives a significant improvement, and the second order cumulant expansion can only be used for very local extrapolations.

The predictions of the enthalpy and heat capacity using the corrected enthalpy fluctuations (not shown) and the full enthalpy fluctuations are of comparable quality. However, the accuracy of the Gamma states for the excess heat function in the *NVT* ensemble is clearly higher (see Refs. 3 and 4), especially for a sensitive property like the heat capacity, and in contrast to the canonical ensemble the use of excess fluctuations in the *NpT* ensemble does not really improve the accuracy.

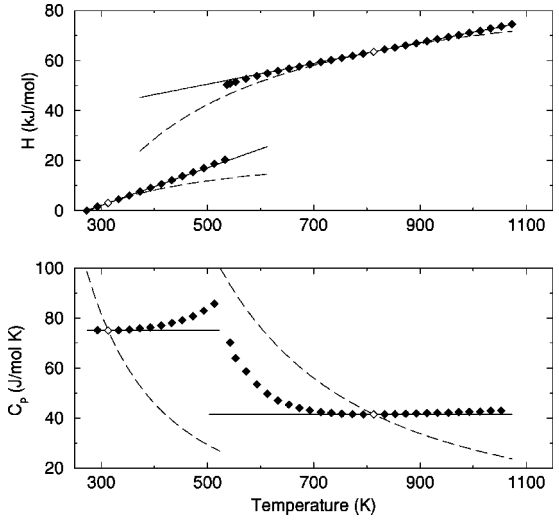

FIG. 2. Enthalpy H and heat capacity C_p along a water isobar at $p=50.0$ bar. Legend: see Fig. 1.

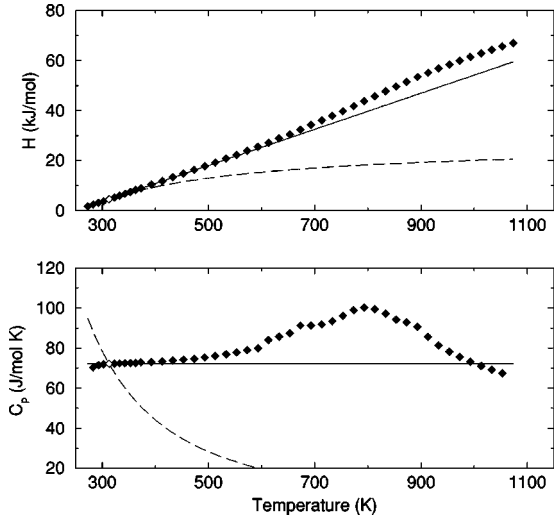

FIG. 4. Enthalpy H and heat capacity C_p along a water isobar at $p=1000.0$ bar. Legend: see Fig. 1.

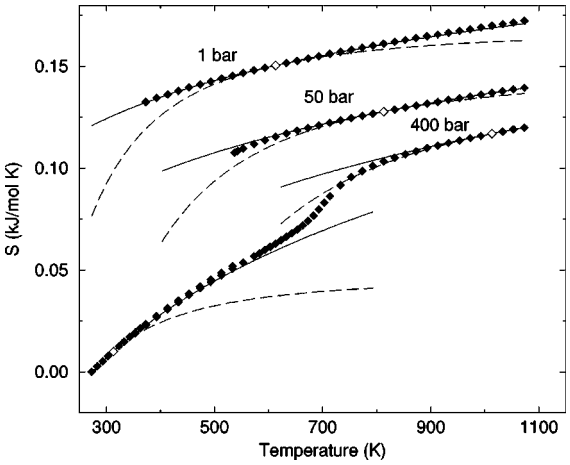

FIG. 5. Entropy S of water along different isobars. Legend: experimental values (♦), diverging Gamma states [Eq. (62)] on the liquid ($p=400$ bar) and gas side (——) and corresponding Gaussian states [Eq. (43)] (— — —). The critical pressure is 221.2 bar (Ref. 39). The values of T_0 for the liquid and gas side are indicated by ◇.

Finally, in Fig. 5 the predictions for the entropy using full enthalpy fluctuations show the same trend as the enthalpy and heat capacity predictions (for clarity only the first three isobars are shown). Also here the predictions using the corrected enthalpy fluctuations (not shown) and the full enthalpy fluctuations have the same accuracy.

V. CONCLUSION

In this article we showed how to extend the quasi-Gaussian entropy theory in an exact way to noncanonical ensembles. We derived general expressions for the solutions of thermodynamic master equations for the temperature dependence in different ensembles, and described specific aspects of the *NpT*, μVT and *NVT* conditions. Gaussian and Gamma statistical states were derived in detail in the new ensembles (*NpT* and μVT) and were applied to describe the thermodynamics of water in gas and liquid conditions.

We first showed that in the *NpT* ensemble an ideal gas can be described in general by a diverging Gamma state for the corrected and full enthalpy fluctuations, suggesting that a diverging Gamma state could be a good description at least of the gas behavior. In contrast to the situation in the canonical ensemble using the energy fluctuations in the *NpT* and μVT ensembles we encounter phase transitions. Following the usual thermodynamic approach (i.e., regarding the phase transitions as singularities) we have for the subcritical isobars two distinct solutions: a gas and a liquid one.

Applying Gaussian and Gamma states, the results clearly show that we can describe a considerable part of the thermodynamics of water using two Gamma state solutions, a low-density (gas) diverging Gamma state, and a high-density (liquid) one, but no single Gamma state can be used as a unique statistical state of the system for all densities, even at supercritical isobars. This implies that for a real system its unique exact solution, able to describe both gas and liquid conditions including phase transitions and the critical point region, is in the *NpT* and μVT ensembles beyond the Gamma level of the theory and hence requires a more complex model statistical state. In the subsequent paper we will present a discussion on the implications of the existence of thermodynamic master equations and phase transitions.

It is interesting to note that in the canonical ensemble[2–4] the use of fluctuations of the excess heat function (ideal reduced internal energy) provides a more accurate description of the thermodynamics. In fact, the Gamma state solutions provide in that case a model along the isochores which can be used over a very large temperature range, even in the critical point region. On the contrary the Gamma state solutions in the *NpT* and μVT ensembles cannot be used as a general model for the temperature dependence of fluid thermodynamics, as they are too simple to describe the fluid behavior at phase transitions or close to the critical temperature. However, when compared to a usual second order cumulant expansion, equivalent to a Gaussian state, these diverging Gamma states clearly show that the use of a physically acceptable Gamma distribution function improves the quality of the model considerably. In fact, the Gaussian state has the same problems concerning phase transitions and the critical point region, but in addition can be used only for very local extrapolations. The diverging Gamma state on the other hand seems to describe the fluid behavior properly in the ''stable'' regions, as shown by the fact that in the ''liquid'' and the ''gas'' ranges of the solution a very sensitive property like the heat capacity is rather constant, as predicted by the diverging Gamma state.

Finally, it should be noted that limitation to the semiclassical limit is not necessary: this theory could be derived from a full quantum description of the partition function as well. However, in the case of an exact quantum description no fluctuations of excess heat functions can be used.

In the subsequent article we will show how to use the QGE theory to derive the density dependence in the *NpT* and μVT ensembles using the volume and particle number distributions.

ACKNOWLEDGMENTS

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APPENDIX

From quantum mechanics we know that any set of phase-space positions which are permutations of identical particles should be considered as a unique physical state and so counted as a single phase-space position in the partition function. Since for a system in the classical limit the canonical partition function can be expressed as the product of two independent integrals, one only on the classical momenta and the other on the classical coordinates,[4] we can obtain a correct evaluation of the partition function by counting any set of configurations which are permutations of identical particles (indistinguishable configurations) as a single configuration. To accomplish this correction in the configurational integral we can decompose the classical degrees of freedom

of the molecule (excluding bond lengths and angles which are considered completely constrained[4]) into translational, rotational and intramolecular ones. Hence for any given configuration of the system we can evaluate the corresponding total number of translations, rotations and intramolecular displacements which are permutations of identical particles as

$$n(\mathbf{x}_{\text{int}}) = N! \prod_{i=1}^{N} (1+\gamma_i(\mathbf{x}_{i,\text{int}})) \qquad \gamma_i = 0,1,2,\ldots, \tag{A1}$$

where $\mathbf{x}_{\text{int}}$ are the classical intramolecular coordinates, $\mathbf{x}_{i,\text{int}}$ the ones of the ith molecule and $1+\gamma_i$ the total number of indistinguishable configurations only due to rotations and intramolecular displacements of the molecule. For macroscopic systems we can safely assume that although each γ_i is in principle a function of the corresponding intramolecular coordinates the product of all the factors $1+\gamma_i$ is virtually identical for every configuration of the system, so

$$\prod_{i=1}^{N} (1+\gamma_i) \cong (1+\gamma)^N \qquad \gamma \geqslant 0, \tag{A2}$$

where γ can be considered a density and temperature independent constant, characteristic of the molecules. Hence, dividing the configurational integral by $N!(1+\gamma)^N$ provides the required correction. For sake of simplicity we always include the factor $(1+\gamma)^{-N}$ into the electronic partition function.

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